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Method for the determination of aromatic amines in workplace air using gas chromatography

Air Monitoring Method

J. Fauss¹
T. H. Brock^{2,*}
R. Hebisch^{3,*}

A. Hartwig^{4,*}
MAK Commission^{5,*}

Keywords

aromatic amines, air analysis, analytical method, workplace measurement, hazardous substances, gas chromatography, inhalable fraction

¹ German Social Accident Insurance Institution for the foodstuffs industry and the catering trade, Dynamostr. 7–11, 68165 Mannheim, Germany

² German Social Accident Insurance, Institution for the raw materials and chemical industry, Prevention – Department of Hazardous Substances, Biological Agents and Analytical Chemistry, Kurfürsten-Anlage 62, 69115 Heidelberg, Germany

³ Chair of the working group “Air Analyses” of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany

⁴ Chair of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Department of Food Chemistry and Toxicology, Institute of Applied Biosciences, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany

⁵ Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Kennedyallee 40, 53175 Bonn, Germany

* E-Mail: T. H. Brock (analytik@bgrci.de), R. Hebisch (luftanalysen-dfg@baua.bund.de), A. Hartwig (andrea.hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)

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Please direct correspondence to Berufsgenossenschaft Rohstoffe und chemische Industrie, Prävention, P.O. Box 101480, 69004 Heidelberg, Germany; analytik@bgrci.de

Abstract

This analytical method is a validated measurement procedure for the determination of 2-methylaniline, 3-methylaniline, 4-methylaniline, 1-naphthylamine, 2-naphthylamine, 2-aminobiphenyl, 3-aminobiphenyl and 4-aminobiphenyl in workplace air averaged over the sampling period after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through two acid impregnated quartz fibre filters using a suitable flow-regulated pump. The flow rate is set to 1 l/min with a recommended air sample volume of 120 l. The collected aromatic amine is desorbed, transferred to an aqueous template, extracted in an alkaline medium with toluene and derivatized with heptafluorobutyric anhydride. The aromatic amine is then analysed by means of gas chromatography and a mass selective detector (MSD). The quantitative evaluation is based on a calibration function obtained by means of a multiple-

point calibration using 1-aminofluorene as internal standard. The limit of quantification (LOQ) for each amine deposited on the filters is between $0.001 \mu\text{g}/\text{m}^3$ and $0.008 \mu\text{g}/\text{m}^3$ based on an air sample volume of 120 l, 2 ml desorption solution and an injection volume of $0.5 \mu\text{l}$. The mean recovery for all tested amines was between 87 and 95% and the expanded uncertainty between 22 and 33%.

This method has been tested and recommended for the determination of aromatic amines in workplaces by the German Social Accident Insurance.

Name	CAS No.	Molar mass
2-Methylaniline; o-toluidine	95-53-4	107.16
3-Methylaniline; m-toluidine	108-44-1	107.16
4-Methylaniline; p-toluidine	106-49-0	107.16
1-Naphthylamine; α -naphthylamine; 1-aminonaphthalene	134-32-7	143.19
2-Naphthylamine; β -naphthylamine; 2-aminonaphthalene	91-59-8	143.19
2-Aminobiphenyl; 2-phenylaniline, 2-biphenylamine	90-41-5	169.23
3-Aminobiphenyl; 3-phenylaniline, 3-biphenylamine	2243-47-2	169.23
4-Aminobiphenyl; 4-phenylaniline, 4-biphenylamine	92-67-1	169.23

Both personal and stationary sampling can be employed for the risk assessment of workplaces.

1 Summary

This analytical method describes the determination of the mean concentration of methylanilines, phenylanilines and naphthylamines, abbreviated to amines in this method, at the workplace over the sampling period using personal or stationary sampling.

Measurement principle:	A pump draws a defined volume of air through a cassette equipped with two acid-impregnated filters. The deposited amines are then transferred to an aqueous solution, extracted with toluene in an alkaline medium and derivatised with heptafluorobutyric anhydride. After gas chromatographic separation, determination is carried out with the mass selective detector.
Limit of quantification:	<p>Absolute: 0.04 to 0.23 pg per amine</p> <p>Relative: 0.001 to $0.008 \mu\text{g}/\text{m}^3$ of amine for an air sample volume of 120 l, a desorption solution of 2 ml and an injection volume of $0.5 \mu\text{l}$</p>
Working range:	Validated in the range of 1.04 to $100 \mu\text{g}/\text{m}^3$ at an air sample volume of 120 l for all the amines, exception: 1-naphthylamine can be determined due to reduced values at low concentrations from $100 \mu\text{g}/\text{m}^3$.
Selectivity:	A very high selectivity is achieved using pH-controlled extraction, the derivatization of the amines, the gas chromatographic separation of the derivatives and the use of a mass selective detector.
Advantages:	Personal and selective measurements are possible at a very high sensitivity.

Disadvantages:	No indication of concentration peaks, relatively elaborate preparation required.
Apparatus:	Sampling system consisting of a pump, flow meter and cassette with acid-impregnated filters, gas chromatograph with mass selective detector.

2 Equipment and chemicals

2.1 Equipment

For sampling:

- Pump with a nominal flow rate of 1 l/min, e.g. SG 2500, from GSA, 40880 Ratingen, Germany
- Flow meter, e.g. Gilibrator from Gilian supplied by DEHA Haan & Wittner GmbH, 71296 Heimsheim, Germany
- Centrifuge vials made of fluorinated ethylene propylene (FEP) with screw caps, 10 ml, e.g. Nalgene supplied by e.g. VWR, 64295 Darmstadt, Germany
- Aluminium foil
- Sample carrier, consisting of two glass fibre filters separately fitted into a polystyrene cassette, diameter of filters 37 mm, each impregnated with 0.5 ml of 0.13 mol/l sulphuric acid; e.g. from SKC supplied by e.g. Analyt-MTC GmbH, 79379 Müllheim, Germany.

Alternatively the glass fibre filter (from Pall) is wetted in a glass dish or in a watch glass with 0.5 ml of 0.13 mol/l sulphuric acid and left to dry overnight in air. Then the filters are fitted into an empty cassette (from SKC). They are stable for at least six months under these conditions. Filter and blank cassettes also supplied by e.g. Analyt-MTC GmbH.

For sample preparation:

- Tweezers
- Benchtop centrifuge with a rate of at least 5000 rpm, e.g. from Hettich GmbH, 78532 Tuttlingen, Germany
- Horizontal shaker with a vibration frequency of at least 420 rpm, e.g. from Bühler GmbH, 72379 Hechingen, Germany
- Test tube shaker with a vibration frequency of at least 2500 rpm, e.g. from IKA-Werke GmbH, 79219 Staufen, Germany
- pH meter, e.g. from WTW, Xylem Analytics Germany GmbH, 82362 Weilheim, Germany
- Automatic positive displacement pipette, e.g. Multipette Xstream, from Eppendorf, 22339 Hamburg, Germany
- Screw-capped vials, 4 ml (amber)

For analytical determination:

- Gas chromatograph with mass selective detector (MSD)
- Volumetric flasks, 5 ml, 10 ml, 100 ml (amber glass)

- Erlenmeyer flask, 100 ml
- Autosampler vials, 1.5 ml (amber)

2.2 Chemicals

- m-Toluidine, purity 99.8%, e.g. from LGC Standards, 46485 Wesel, Germany
- p-Toluidine, purity 99.5%, e.g. from LGC Standards
- 2-Aminobiphenyl, purity 99%, e.g. from LGC Standards
- 3-Aminobiphenyl, purity 99.9%, e.g. from LGC Standards
- Amine mix, e.g. from LGC Standards: including, amongst others, 2000 µg/ml each of o-toluidine, 1-naphthylamine, 2-naphthylamine and 4-aminobiphenyl in dichloromethane
- 1-Aminofluorene, purity 99% as an internal standard (ISTD), e.g. from Sigma-Aldrich, 82024 Taufkirchen, Germany
- Toluene, p.a., e.g. from Merck, 64293 Darmstadt, Germany
- Sodium hydroxide, e.g. from Merck
- Sodium hydroxide, 0.5 mol/l, e.g. from Merck
- Heptafluorobutyric anhydride (HFBA), purity 99%, e.g. from Sigma-Aldrich
- Potassium dihydrogen phosphate, e.g. from Sigma-Aldrich
- Ultrapure water, e.g. from Merck
- Sulphuric acid, concentrated, e.g. from Merck
- Helium 5.0, purity 99.999%

Phosphate buffer: 1 mol/l potassium dihydrogen phosphate solution, pH 7

13.6 g of potassium dihydrogen phosphate are weighed into a 100 ml Erlenmeyer flask and water is added to reach approx. 90 ml. It is then adjusted to a pH-value of 7 with concentrated sodium hydroxide and filled with water to 100 ml.

Sulphuric acid: Diluted sulphuric acid, 0.13 mol/l

A pipette is used to add 722 µl of concentrated sulphuric acid (96%) into a 100 ml volumetric flask into which several ml of water have been previously placed. Then the flask is filled to the mark with water and shaken.

ISTD stock solution: Solution of approx. 570 µg/ml of 1-aminofluorene in toluene

Approx. 5.7 mg of 1-aminofluorene are weighed exactly to the nearest 0.1 mg in a 10 ml volumetric flask. Then the flask is filled to the mark with toluene and shaken.

Desorption solution: Solution of approx. 500 ng/ml of 1-aminofluorene in toluene

A pipette is used to add approx. 90 µl of the ISTD stock solution into a 100 ml volumetric flask into which several ml of toluene have been previously placed and the flask is filled to the mark with toluene and shaken.

Stock solutions 1: Four solutions of approx. 2000 µg amine/ml toluene (see Table 1)

The amines listed in Table 1 are separately weighed to the nearest 0.1 mg into a 10 ml amber volumetric flask. Then the flask is filled to the mark with toluene and shaken.

Tab. 1 Masses and concentrations of the amines in stock solutions 1

Substance	Mass [mg]	Concentration [µg/ml]
m-Toluidine	20.0	2000
p-Toluidine	20.1	2000
2-Aminobiphenyl	20.2	2000
3-Aminobiphenyl	20.0	2000

Stock solution 2: Solution of approx. 5.0 µg amine/ml desorption solution

Some ml of the desorption solution were placed into a 20 ml amber volumetric flask and then 50 µl of each of the stock solutions 1 (see Table 1) and 50 µl of the amine mix were added. The amine mix (see Section 2.2) contains, amongst others, the compounds o-toluidine, 1-naphthylamine, 2-naphthylamine and 4-aminobiphenyl with a concentration of 2000 µg/ml each. Then the volumetric flask is filled up to the mark with desorption solution and shaken.

Calibration solutions: Solutions of approx. 20 to 500 ng amine/ml desorption solution (see Table 2)

The seven volumes of stock solution 2 listed in Table 2 are each pipetted into a 10 ml amber volumetric flask, into which several ml of desorption solution have been previously placed, then the flask is filled with desorption solution and shaken.

Tab. 2 Concentrations of the amines in the calibration solutions in ng/ml

Solution	1	2	3	4	5	6	7
Addition of stock solution 2 in µl	40	200	360	520	680	840	1000
o-Toluidine	20	100	180	260	340	420	500
m-Toluidine	20	100	180	260	340	420	500
p-Toluidine	20	100	180	260	340	420	500
1-Naphthylamine	20	100	180	260	340	420	500
2-Naphthylamine	20	100	180	260	340	420	500
2-Aminobiphenyl	20	100	180	260	340	420	500
3-Aminobiphenyl	20	100	180	260	340	420	500
4-Aminobiphenyl	20	100	180	260	340	420	500
1-Aminofluorene	500	500	500	500	500	500	500

1 ml each of the calibration solutions is used according to Section 4.1 for the derivatization.

A concentration range from 0.333 to 8.33 $\mu\text{g}/\text{m}^3$ of individual substance is covered (see Table 3) by these solutions, based on an air sample volume of 120 l.

Tab. 3 Converted concentrations of the amines in the calibration solutions in mg/m^3 (based on an air sample volume of 120 l)

Solution	1	2	3	4	5	6	7
o-Toluidine	0.333	1.67	3.00	4.33	5.67	7.00	8.33
m-Toluidine	0.333	1.67	3.00	4.33	5.67	7.00	8.33
p-Toluidine	0.333	1.67	3.00	4.33	5.67	7.00	8.33
1-Naphthylamine	0.333	1.67	3.00	4.33	5.67	7.00	8.33
2-Naphthylamine	0.333	1.67	3.00	4.33	5.67	7.00	8.33
2-Aminobiphenyl	0.333	1.67	3.00	4.33	5.67	7.00	8.33
3-Aminobiphenyl	0.333	1.67	3.00	4.33	5.67	7.00	8.33
4-Aminobiphenyl	0.333	1.67	3.00	4.33	5.67	7.00	8.33

3 Sampling

The polystyrene cassette fitted with two acid-impregnated glass fibre filters is connected to the pump ensuring that it is correctly orientated (the part labelled ‘inlet’ is directed towards the area to be sampled). The flow rate is adjusted to 1 l/min. The pump and the sampling system are either worn by a person at the workplace or stationary sampling is carried out. The method was tested up to a sample volume of 120 l (equivalent to a sampling period of 120 minutes). The requirements for sampling the inhalable fraction are met by the combination of the flow rate and the geometry of the sampling system. After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than $\pm 5\%$, it is advisable to repeat the sampling (see DGUV Information 213-500 “General Part” (DGUV 2015)). The cassette is subsequently tightly sealed with the sealing plugs.

Further process steps are dependent on the amines to be determined (see Section 6.3).

If the filters can remain in the cassettes, they must be stored protected from light and dispatched to the investigating laboratory according to the guidelines set out in Section 6.3, where they must be transferred into the aqueous solution while observing the maximum storage period (see below).

Otherwise both the filters are removed from the cassette and each filter is placed in a vessel (centrifuge vial filled with 2 ml of water) immediately after sampling or at the latest after 4 hours. For this purpose, the cassette is prised open and the filter is transferred using tweezers (control filter first), whereby it must be ensured that the filter is entirely wetted in the sample vessel. The sample vessel is then wrapped in aluminium foil and is made available to the laboratory according to the specifications in Section 6.3.

4 Analytical determination

4.1 Sample preparation

In the laboratory after prising open the cassette, the glass fibre filters still in the sample carrier are each transferred to a separate aqueous solution (centrifuge vial filled with 2 ml of water) and completely wetted (see above). 1 ml of 0.5 N sodium hydroxide is added to the samples in the same manner as the filters dispatched in the aqueous solutions. Then a pipette is used to add exactly 2 ml of desorption solution. After each addition, the vessel is briefly

shaken. The vessel is sealed and initially shaken for approx. 20 seconds by means of a test-tube shaker adjusted to the highest setting. Then it is shaken for 20 minutes on the horizontal shaker. Then the sample vessels are centrifuged for 10 minutes at 5000 rpm. 1 ml of the supernatant organic phase is then withdrawn using a pipette and transferred to a 4 ml amber screw-capped vial.

25 µl of heptafluorobutyric anhydride are added to 1 ml each of calibration solution (Table 2) or sample extract in the 4 ml amber screw-capped vial and the vial is shaken intensively for 20 seconds in the test-tube shaker. After a derivatization period of at least 10 minutes, 1 ml of phosphate buffer is added to each solution. Subsequently the solution is again shaken intensively for 20 seconds (the solution must be milky white). After the phases have separated, an aliquot of the supernatant organic phase (sample solution) is transferred to an amber autosampler vial.

In order to ensure that the solutions and filters used do not contain any interfering impurities, an acid-impregnated filter is placed into 2 ml of water and included in each sample series. Then, sodium hydroxide followed by desorption solution are added, as described above. The extraction, derivatization and purification of the extract are also carried out as described above (blank solution).

0.5 µl of the sample solution and 0.5 µl of the blank solution are injected into the gas chromatograph and a gas chromatogram is recorded as described below.

4.2 Operating conditions

The characteristics of the method stated in Section 6 were obtained under the following operating conditions:

Apparatus: HP 6890A gas chromatograph with 5973 Network MSD mass specific detector, and PTV injector, from Agilent, 76337 Waldbronn, Germany

GC parameters:

Separation column: Fused silica capillaries; stationary phase: 50% phenyl/50% methylpolysiloxane, e.g. DB-17 ms, inner diameter 0.25 mm, length 30 m, film thickness 0.25 µm, e.g. from Agilent

Injection: 0.5 µl; splitless for 1 min, injector temperature: 250 °C

Oven program: Initial temperature: 55 °C for 2 min
Heating rate I: 10 °C/min until 250 °C
Heating rate II: 16 °C/min to 270 °C, 5 min isothermal

Carrier gas: Helium 130 kPa pre-pressure (constant pressure)

Transfer line: 250 °C

MSD parameters:

Ionisation type: EI (70 eV)

Measurement mode: SIM (recorded masses, see Table 4)

Dwell time: 60 to 80 ms

Measurement in time intervals: [Toluidines], [2-aminobiphenyl], [naphthylamines], [3- and 4-aminobiphenyl], [1-aminofluorene]

Tab. 4 SIM recorded masses (m/z) for the quantification (target ion) and qualification (qualifier ions, with indication of their signal intensities in regard to the target ion in %)

Substance	Target	Qualifier 1	Intensity	Qualifier 2	Intensity
2-Methylaniline – HFBA-amide	303	134	100	106	32
3-Methylaniline – HFBA-amide	303	134	39	106	23
4-Methylaniline – HFBA-amide	303	134	23	106	39
1-Naphthylamine – HFBA-amide	339	115	42	142	30
2-Naphthylamine – HFBA-amide	339	115	44	142	36
2-Aminobiphenyl – HFBA-amide	365	366	19	168	13
3-Aminobiphenyl – HFBA-amide	365	366	20	168	15
4-Aminobiphenyl – HFBA-amide	365	366	18	168	42
1-Aminofluorene – HFBA-amide	377	165	32	–	–

5 Evaluation

5.1 Calibration

In each case 0.5 µl of the calibration solutions described in Section 2.2 and the calibration solutions derivatized as described in Section 4.1 are injected into the gas chromatograph.

The ratios of the peak areas of the amine derivatives to the peak areas of the derivative of 1-aminofluorene (ISTD) are plotted versus the corresponding mass ratios obtained from the calibration solutions. The calibration functions are calculated by means of linear regression.

5.2 Calculation of the analytical result

The peak areas of the amine derivatives and of the 1-aminofluorene derivative are obtained from the resulting chromatograms, the quotient is calculated and the corresponding value for the mass in the sample solution in ng is determined from the relevant calibration function.

The mass concentration of each individual substance in the air sample in µg/m³ is calculated using Equation 1:

$$c = \frac{m \cdot f}{V \cdot \eta} \quad (1)$$

where:

c is the mass concentration of the respective amine in the sample air in µg/m³

m is the sum of masses of the amine in both sample solutions from the collection and control filter obtained from the corresponding calibration function in ng

- f is the aliquot factor, without the dilution step, in this case $f = 2$
- V is the air sample volume in litres
- η is the recovery (see Section 6.1)

If the resulting content of the individual amine derivative is outside the calibration range, then the derivatization must be repeated with a lower extract volume. For example, in order to obtain a dilution by a factor of four, desorption solution is added to 250 μl of the original sample extract to obtain a volume of 1 ml and it is then used for derivatization (in this case $f = 8$).

6 Reliability of the method

6.1 Precision and recovery

The precision in the lowest measurement range and the recovery were determined according to DIN EN 482 for three concentrations (DIN 2015). The validation solutions were prepared according to the data listed in Table 5:

- Validation solutions 1 to 3:** Solutions of 2.5 mg/l, 20 mg/l and 240 mg/l of amines in toluene
- The following were placed into 5 ml amber volumetric flasks:
- 6.25 μl each of the four stock solutions 1 and 6.25 μl of the amine mixture (validation solution 1)
 - 50 μl each of the four stock solutions 1 and 50 μl of the amine mixture (validation solution 2)
 - 600 μl each of the four stock solutions 1 and 600 μl of the amine mixture (validation solution 3)
- The flasks were filled to the mark with toluene and shaken.

The upper impregnated glass fibre filter in the polystyrene cassette was spiked with 50 μl each of the validation solutions using a microlitre syringe. After an interval of one hour, laboratory air was drawn through the sample carrier at a flow rate of 1 l/min for 120 minutes at an ambient temperature of 22 °C and a humidity of approx. 55%. The preparation, derivatization and analytical determination were carried out as described in Section 4.

1 ml aliquots of the validation solutions, which were diluted in a ratio of 1:40 with desorption solution, derivatised according to Section 4.1 in the same manner as the calibration solutions and purified with buffer solution, served as a reference.

Based on an air sample volume of 120 l, the masses used are equivalent to the stated validation concentrations (see Table 5).

Tab. 5 Concentrations of amines for validation

Substance	Spiked mass			Validation concentration		
	c ₁ [µg]	c ₂ [µg]	c ₃ [µg]	c ₁ [µg/m ³]	c ₂ [µg/m ³]	c ₃ [µg/m ³]
o-Toluidine	0.125	1.0	12.0	1.04	8.33	100
m-Toluidine	0.125	1.0	12.0	1.04	8.33	100
p-Toluidine	0.125	1.0	12.0	1.04	8.33	100
1-Naphthylamine	0.125	1.0	12.0	1.04	8.33	100
2-Naphthylamine	0.125	1.0	12.0	1.04	8.33	100
2-Aminobiphenyl	0.125	1.0	12.0	1.04	8.33	100
3-Aminobiphenyl	0.125	1.0	12.0	1.04	8.33	100
4-Aminobiphenyl	0.125	1.0	12.0	1.04	8.33	100

The relative standard deviations and recoveries (quotient of the spiked mass on the filter and the reference after the suction process) shown in Table 6 were obtained when the procedure described above was carried out at least six times in each case.

Even at the highest validation concentration, the amine masses on the filter connected downstream were less than 1%, based on the total mass of an amine.

Tab. 6 Precision and recovery for the validation of the amines

Substance	Recovery				Relative standard deviation [%]			
	c ₁	c ₂	c ₃	Ø	c ₁	c ₂	c ₃	Ø
o-Toluidine	0.88	0.85	0.92	0.88	4.0	3.5	3.7	3.7
m-Toluidine	0.90	0.87	0.92	0.90	4.4	3.4	3.6	3.8
p-Toluidine	0.87	0.85	0.91	0.87	4.5	3.5	3.8	3.9
1-Naphthylamine	(0.06)	(0.49)	0.89	Trend	(24.9)	(12.7)	3.6	–
2-Naphthylamine	0.75	0.89	0.94	Trend	3.9	2.2	3.8	3.3
2-Aminobiphenyl	0.99	0.91	0.95	0.95	3.0	2.2	4.0	3.1
3-Aminobiphenyl	0.93	0.90	0.93	0.92	2.6	2.1	4.1	2.9
4-Aminobiphenyl	0.88	0.89	0.95	0.91	2.0	2.0	4.0	2.7

In the case of the naphthylamines the data indicate that the recoveries are concentration-dependent. While the analytical results can generally be calculated using the mean value of the recovery in Equation 1, the latter is dependent on the measurement value in the case of 2-naphthylamine. 1-Naphthylamine can be determined only above 100 µg/m³ with this method, which is equivalent to a tenth of its currently valid Occupational Exposure Limit (AGS 2017).

6.2 Limit of quantification

The limits of quantification were determined according to DIN 32645 (DIN 2008) by means of a 10-point calibration in the concentration range of 0.08 to 0.8 ng/ml for a statistical certainty of 95% and a relative uncertainty of 33.3% (k=3).

Based on the respective amine, the limits of quantification of the individual HFBA derivatives were between 0.16 and 0.90 ng per filter. The absolute quantification limits are between 0.04 and 0.23 pg. This is equivalent to relative

limits of quantification of 0.001 to 0.008 $\mu\text{g}/\text{m}^3$ (see Table 7) at an air sample volume of 120 l and a desorption agent volume of 2 ml.

Tab. 7 Limits of quantification of the amines

Substance	Limits of quantification		
	Absolute [pg]	Mass [ng/filter]	Relative [$\mu\text{g}/\text{m}^3$]
o-Toluidine	0.16	0.64	0.005
m-Toluidine	0.08	0.32	0.003
p-Toluidine	0.05	0.20	0.002
1-Naphthylamine	0.23	0.90	0.008
2-Naphthylamine	0.12	0.48	0.004
2-Aminobiphenyl	0.07	0.28	0.002
3-Aminobiphenyl	0.04	0.16	0.001
4-Aminobiphenyl	0.07	0.26	0.002

6.3 Storage stability

The storage stability of the encapsulated filters loaded with 50 μl of validation solution 2 was investigated. Furthermore, the storage stability of the amines on the filter was checked, when it was kept in the aqueous solution. Depending on the amines to be investigated, it is necessary to comply with different storage conditions (see Table 8). Storage stability is considered to be satisfactory, if the loss of analyte is less than 10%.

Tab. 8 Storage stability of the amines

Substance	Filter in the cassette		Filter in aqueous solution	
	Room temperature	4 to 8 °C	Room temperature	4 to 8 °C
Toluidines	7 d	–	14 d	–
1-Naphthylamine	4 h	–	–	7 d
2-Naphthylamine	1 d	7 d	14 d	–
Aminobiphenyls	7 d	–	14 d	–

It was shown that the toluidines and aminobiphenyls may remain on the filter in the sealed capsule for up to one week at room temperature. After transfer into the aqueous solution, the solutions are stable for 2 weeks.

2-Naphthylamine should be transferred to the aqueous solution after one day or if the capsule is refrigerated after one week at the latest, in which case a storage stability of a further 2 weeks can be ensured.

If 1-naphthylamine is to be analysed, immediate transfer of the filters to the aqueous solution is required: the storage period of 4 h must not be exceeded. Furthermore, the aqueous solution must be chilled when dispatched to the investigating laboratory, as considerable losses were detected after only 3 days at room temperature.

Therefore, if 1-naphthylamine does not have to be determined, transfer of the filters by the person carrying out the sampling can be avoided, if the samples are correctly stored.

The samples must be stored protected from light; the sample carriers and aqueous solution should be kept in the refrigerator in the investigating laboratory to minimise losses during storage. Only the analysis of 1-naphthylamine requires sample preparation to be as swift as possible.

6.4 Selectivity

Very high selectivity is achieved using pH-controlled extraction, derivatization of the amines, gas chromatographic separation of the derivatives and a mass selective detector.

6.5 Uncertainty

The expanded uncertainty was estimated taking all relevant influencing factors into consideration as stipulated in DIN EN 482 (DIN 2015) and DIN EN 1076 (DIN 2010). The uncertainty of the entire method and thus also of the analytical result consists principally of the uncertainty contributions of the air sample volume (taking the sampling effectiveness for the inhalable fraction into consideration), the extraction volume, the recoveries and the influences on the measurement values, in particular the scatter of the calibration function and the laboratory's own reproducibility (precision).

The individual uncertainty contributions determined in the bottom-up method are shown in Table 9. As the uncertainties of the measurement (unit: ng/ml) are dependent on their values, they were classed as high, medium and low (equivalent to calibration levels of 7, 4 and 2; see also Tables 2 and 3).

Tab. 9 Uncertainty contributions of the amines in %

Amine	Air sample volume	Extraction volume	Sample storage	Measurement value		
				High	Medium	Low
o-Toluidine	9.2	0.9	3.3	8.0	6.9	10.2
m-Toluidine			3.2	7.1	7.0	10.3
p-Toluidine			4.5	8.2	7.0	11.1
1-Naphthylamine			4.8	7.5	–	–
2-Naphthylamine			5.2	9.8	8.3	13.7
2-Aminobiphenyl			2.6	9.6	8.7	12.8
3-Aminobiphenyl			3.3	8.7	5.5	10.1
4-Aminobiphenyl			4.8	9.9	5.3	11.6

The limitations in terms of storage for both the naphthylamines outlined in Section 6.3 were taken into consideration. With the exception of the naphthylamines, the recovery value was based on the mean value of the 3 recovery experiments (see Table 6) in each case.

The individual uncertainty contributions yielded the substance-dependent and concentration-dependent values for the combined and expanded uncertainties listed in Table 10.

Tab. 10 Determination of the expanded uncertainties of the entire procedure in %

Amine	Combined uncertainty analysis result			Expanded uncertainty analysis result		
	High	Medium	Low	High	Medium	Low
o-Toluidine	11.5	11.3	13.7	23	23	27
m-Toluidine	11.4	11.3	13.7	23	23	27
p-Toluidine	12.0	11.8	14.8	24	24	30
1-Naphthylamine	12.8	–	–	26	–	–
2-Naphthylamine	14.4	13.4	17.3	29	27	35
2-Aminobiphenyl	13.5	12.9	16.0	27	26	32
3-Aminobiphenyl	11.4	11.0	13.9	23	22	28
4-Aminobiphenyl	11.9	11.5	14.6	24	23	29
Corresponding concentration in $\mu\text{g}/\text{m}^3$	100	8.3	1.0	100	8.3	1.0

Therefore, the expanded uncertainty is between 22% and 33% for all the amines. The corresponding concentration of the analysis result is obtained after a sampling period of 2 hours.

7 Remarks

The method described here is based on both OSHA method 73 (toluidines) and OSHA method 93 (naphthylamines, 4-aminobiphenyl), which, however, do not include an internal standard, see OSHA (1988) and OSHA (1992).

In order to meet health and safety requirements, it is recommended that particularly substances that are carcinogenic, mutagenic or toxic to reproduction (CMR substances) are not weighed out, but instead to use commercially available stock solutions (generally in mixtures with other amines).

Higher humidity (75% relative humidity) led to markedly improved recoveries, especially at lower concentrations of the amines; this applies in particular to both the naphthylamines.

The common 5% phenyl/95% methylpolysiloxane phase can also be used as a separation column; in this case, however, the derivatives of 2-aminobiphenyl and 1-naphthylamine elute in reverse order.

Some of the aromatic amines (toluidines, 1-naphthylamine) are sensitive to light, therefore it is advisable to use amber glass vessels and to store the substances in the dark.

The use of the GSP system resulted in a distinct decline of the recovery rates in comparison to the polystyrene cassettes, particularly in the case of the CMR substances 2-naphthylamine and 4-aminobiphenyl. Storage of the filters in the GSP capsules also proved to be unsuitable. Furthermore, a breakthrough cannot be ruled out at higher amine concentrations (greater than $0.1 \text{ mg}/\text{m}^3$).

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Appendix

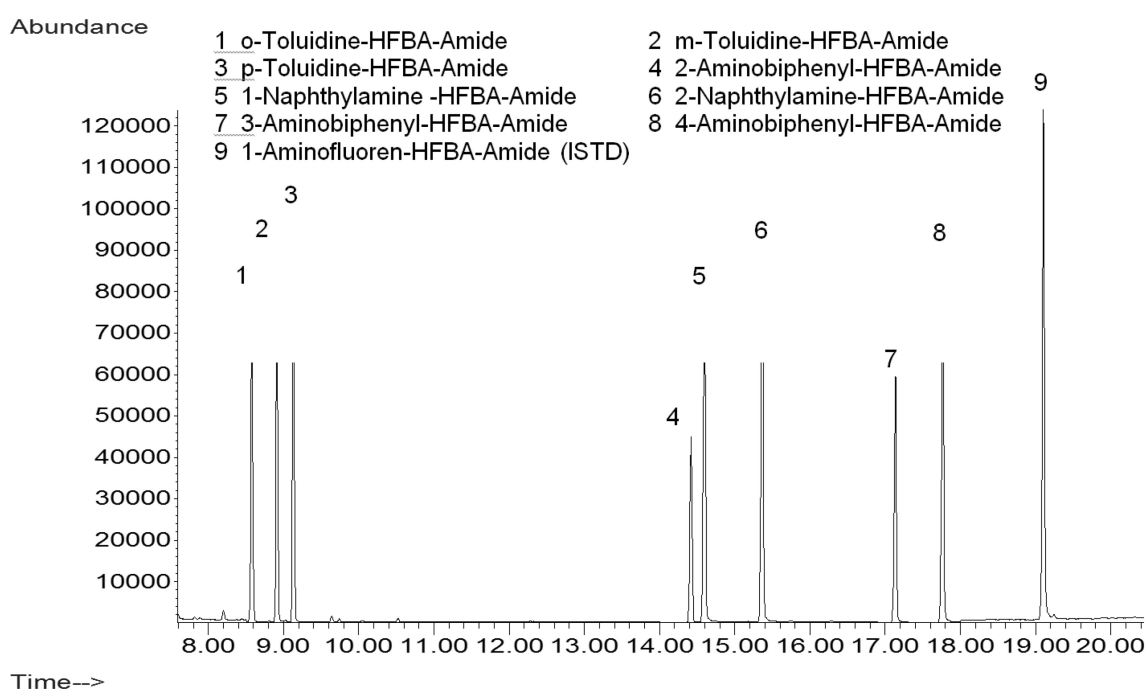


Fig. 1 Chromatogram of calibration solution 4 (260 $\mu\text{g/l}$ per component)

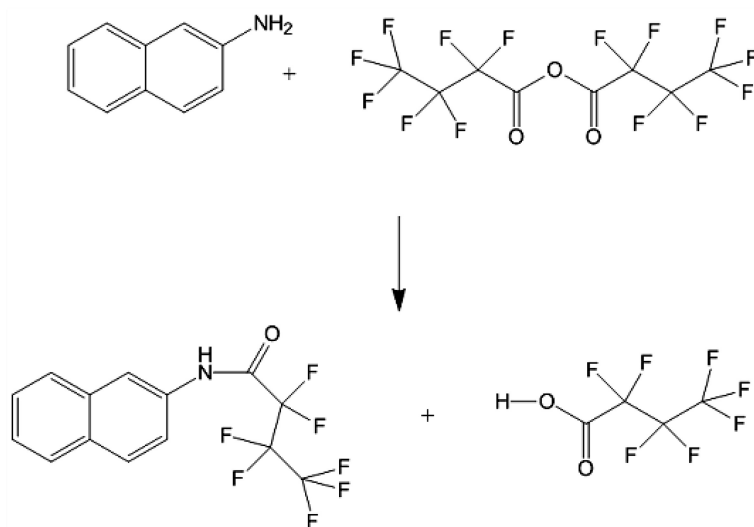


Fig. 2 Derivatization reaction taking 2-naphthylamine as an example

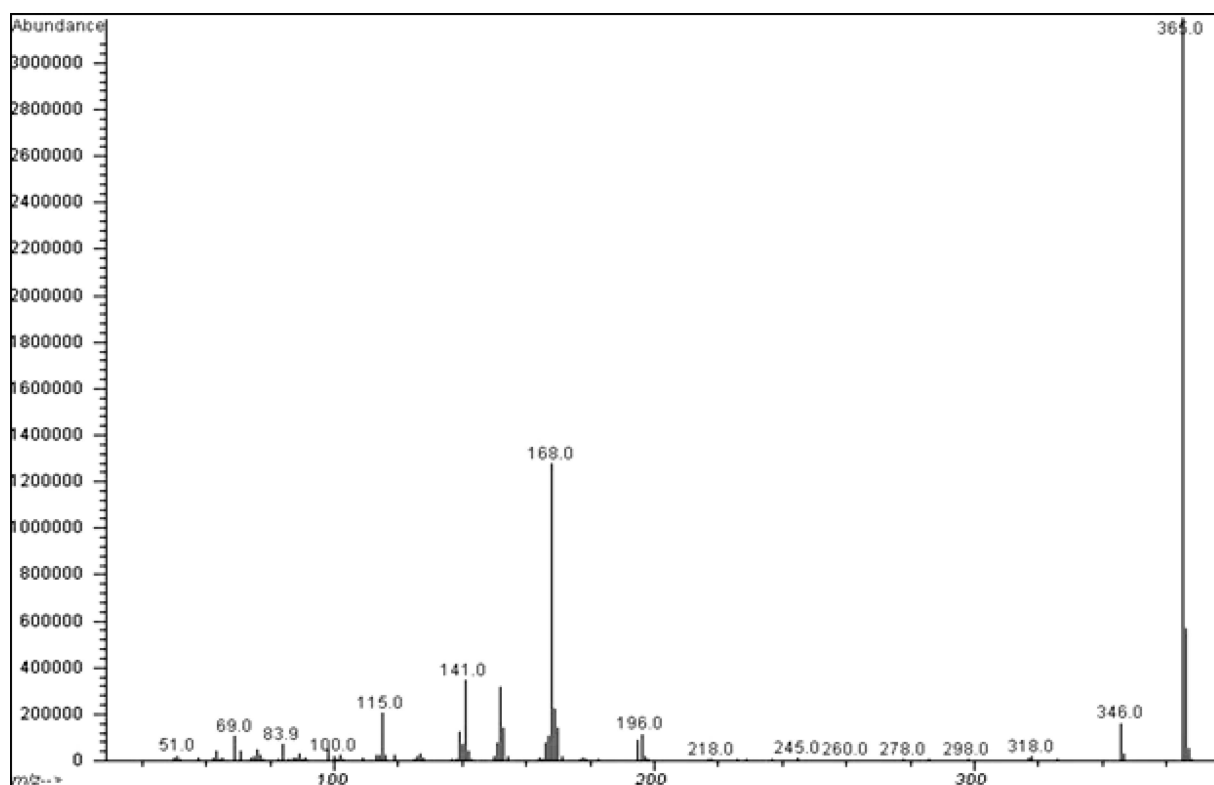


Fig. 3 Mass spectrum of the 2-aminobiphenyl-HFBA derivative